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R&D strategies and related activities beyond Li-ion batteries for EESS

May. 17th, 2017

Battery Research Center,
Korea Electrotechnology Research Institute
Sang-Min Lee

Requirement of large scaled battery

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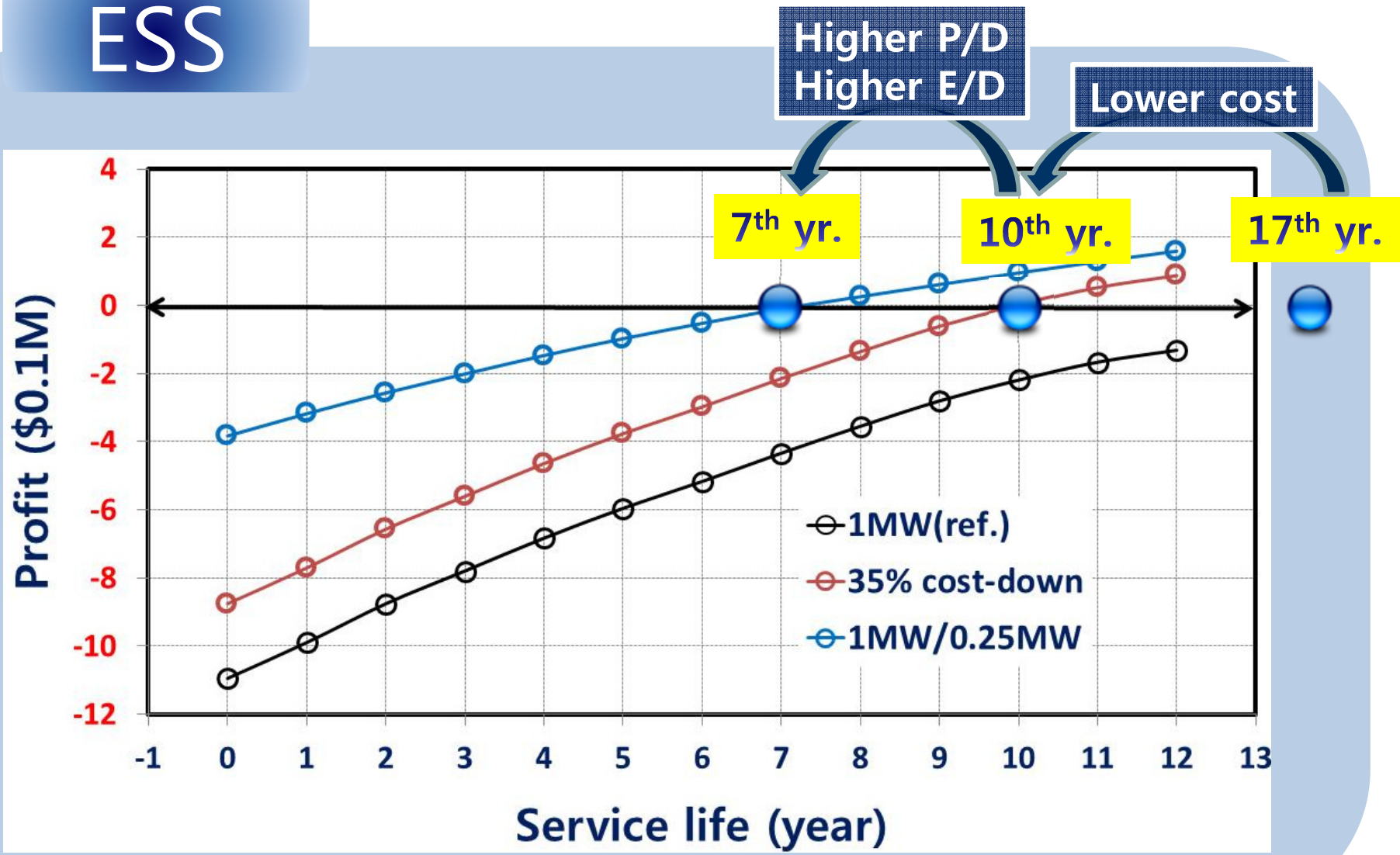
ESS



$/kWh (I) : Higher Li storage chemistry

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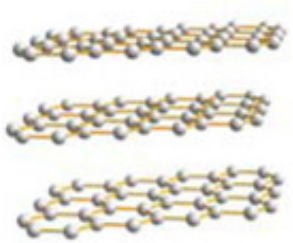
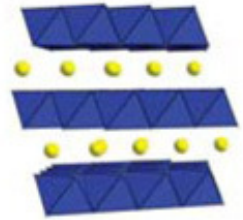
Li-ion battery (LIB)
(Na-Ion battery)

Framework reaction
(Intercalation reaction)



Graphite

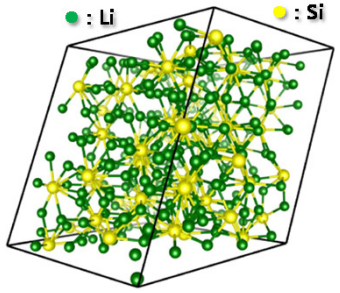
Li_xC (x=1/6, 372mAh/g)



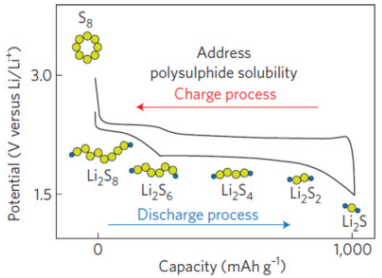
Li_xCoO_2 (x=1, 274mAh/g)

Advanced LIB
Li-Sulfur battery

Framework change reaction
(Conversion reaction, bulk reaction)



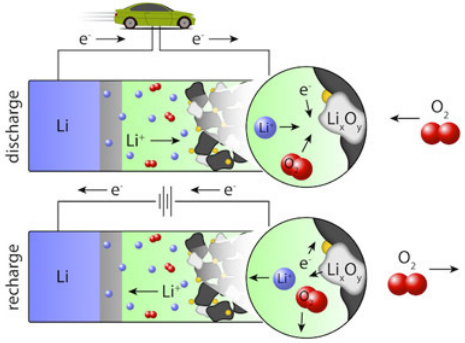
Li_xSi (x=4.4, 4200mAh/g)



Li_xS (x=2, 1672mAh/g)

Li-Air battery

Surface reaction
(3-phases reaction)



Li_xO_2 on carbon
(x=2, ~3000mAh/g of C)

Electrode materials for advanced LIB

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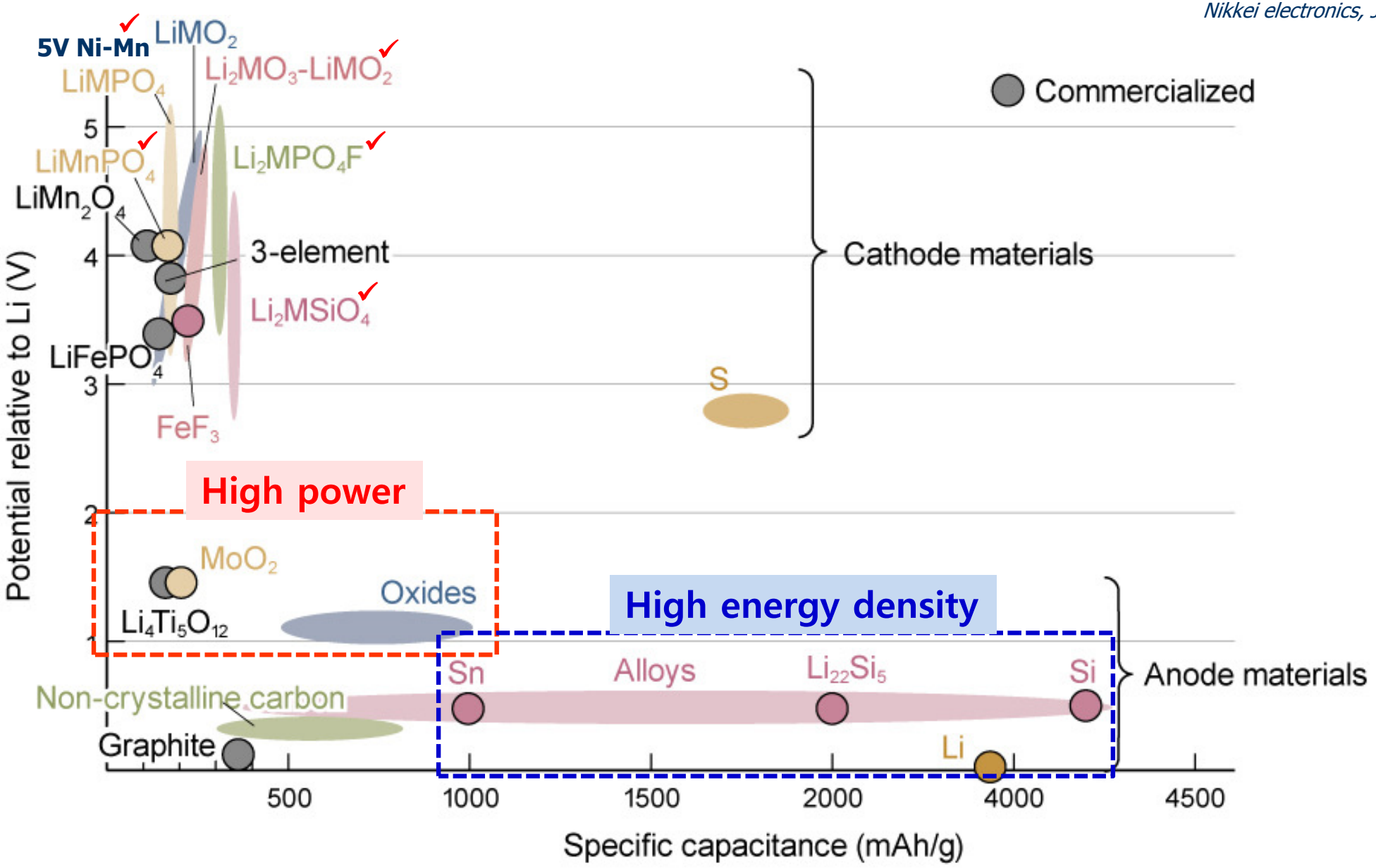
Nikkei electronics, Jan. 2010



$/kWh (II) : Lower cost

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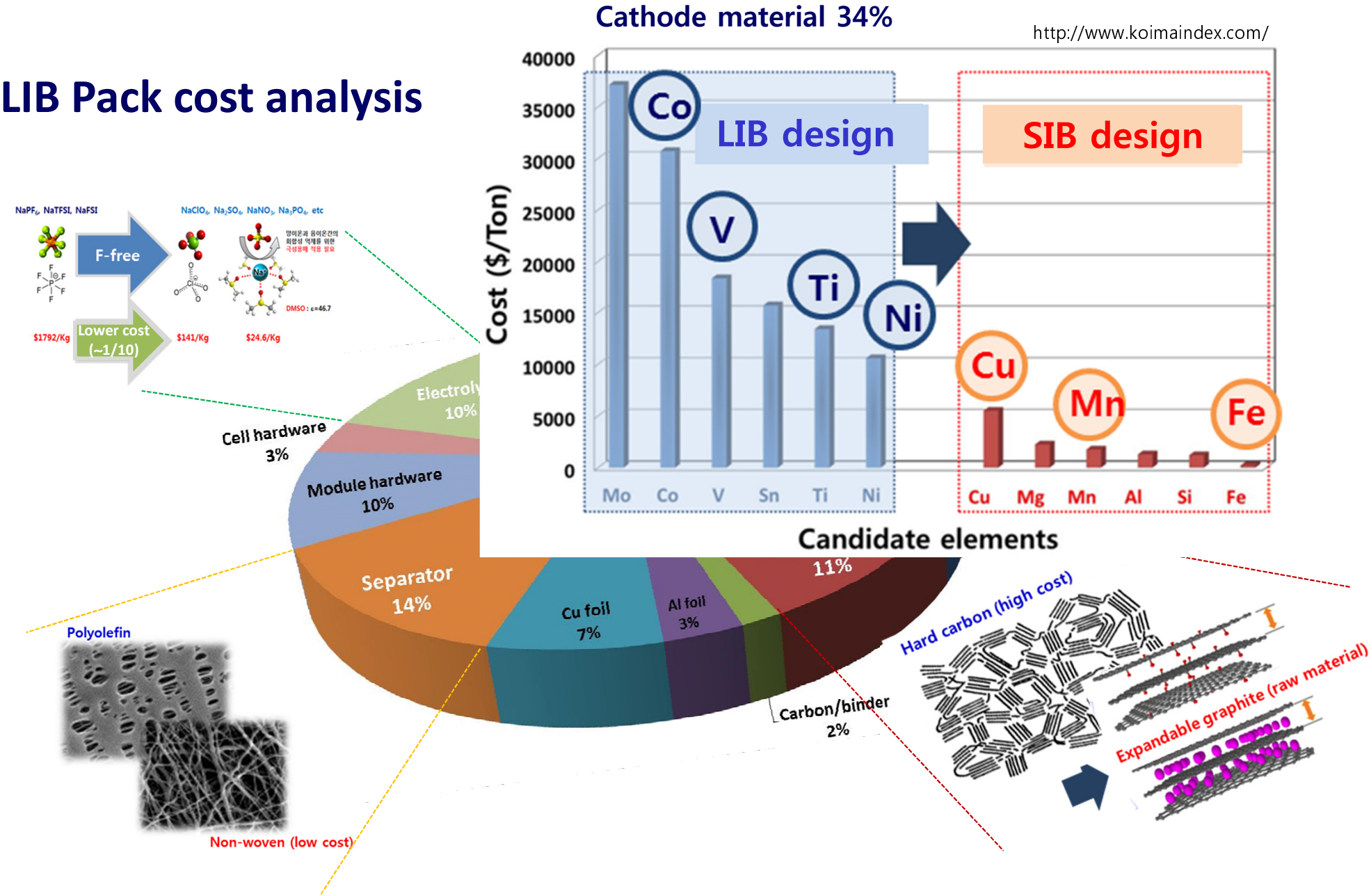
LIB Pack cost analysis



R&D strategy (II) in KERI

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Sodium-ion battery design for low cost

Energy Environ. Sci., 2012, 5, 5884–5901/Chem. Rev. 2014, 114, 11636-11682

	Lithium	Sodium
Cation radius	68pm	**97pm**
Atomic weight	6.9g/mol	**23g/mol**
E_0 vs. SHE	-3.045V	**-2.714V**
Theo. Cap. of $ACoO_2$, mass/vol.	274 $mAhg^{-1}$/1378 $mAhcm^{-3}$	235 $mAhg^{-1}$/1193 $mAhcm^{-3}$
A-O coordination	Octahedral or tetrahedral	Octahedral or prismatic
Melting point	180.5°C	97.7°C

Cathode (Low cost & structural stabilization)

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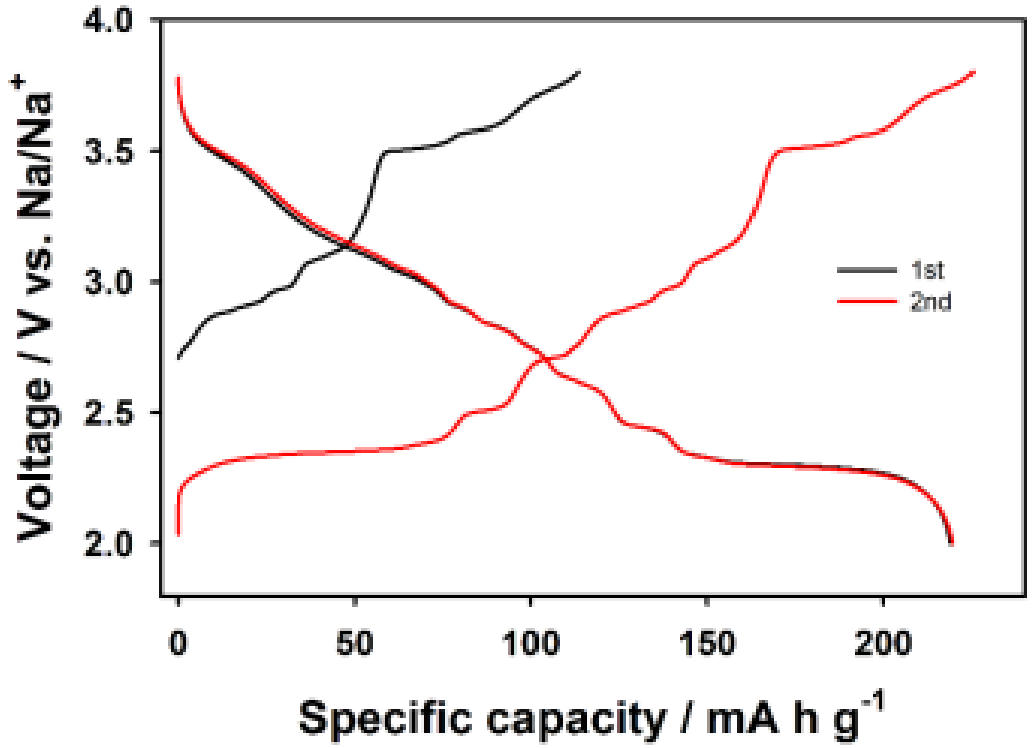
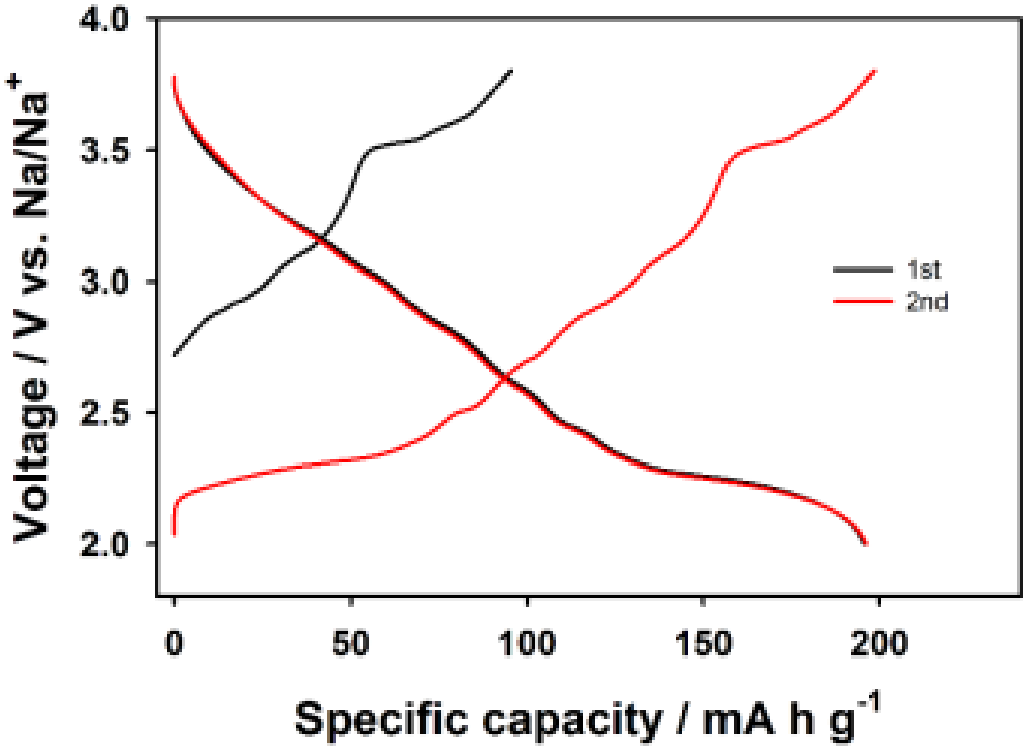
$Na_{0.7}[Mn^{III}_{0.7}Mn^{IV}_{0.3}]O_2$



$Na_{0.7}[Mn^{III}_{0.7-x}Mn^{IV}_{0.3+x}Li_x]O_{2+y}$



ACS Appl. Mater. Interfaces, just accepted, 2017

Cathode (Low cost & structural stabilization)

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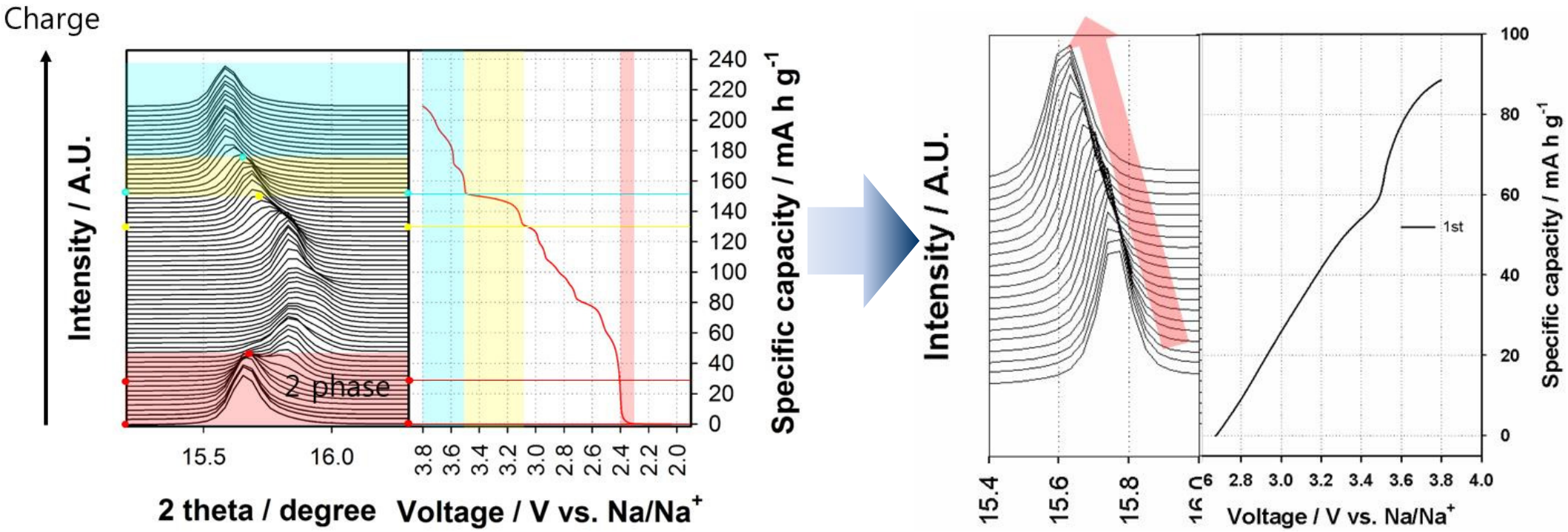
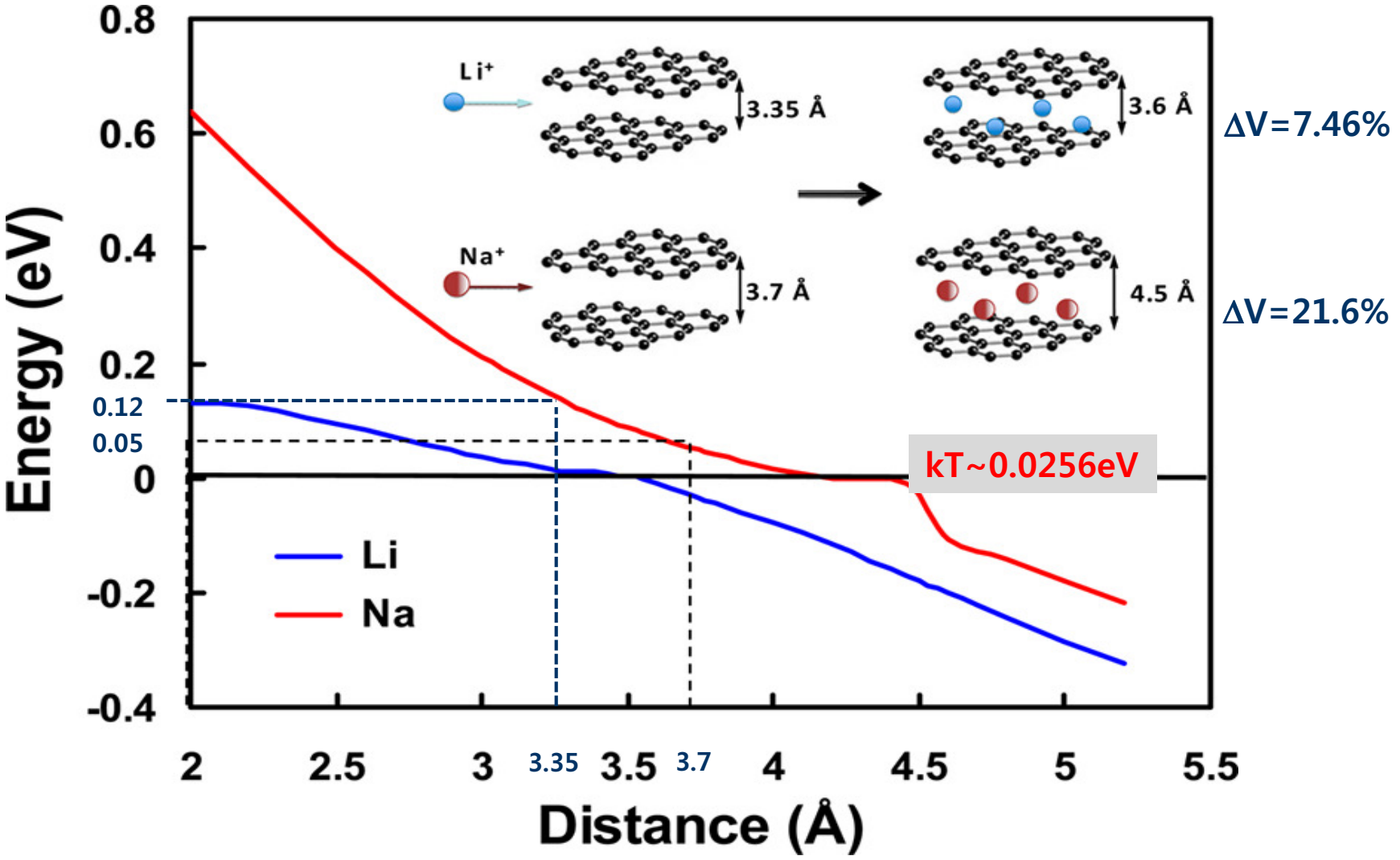


ACS Appl. Mater. Interfaces, just accepted, 2017

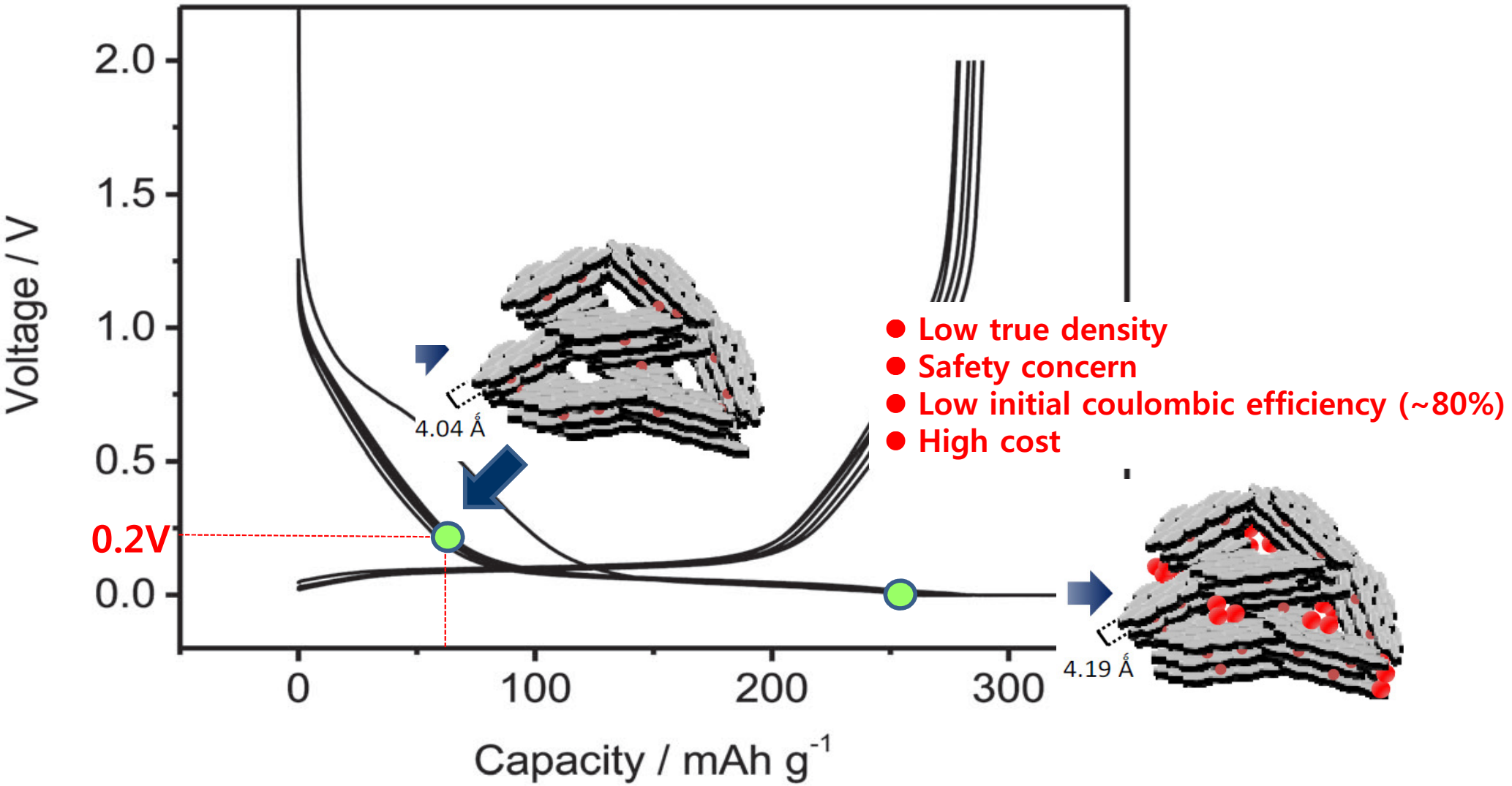
Anode (Graphite)



Nano Lett. 12, 3783–3787 (2012).

Anode (Hard Carbon)

- Sodium is inserted in two different sites between misaligned graphene sheets.
- Nanopores included in hard carbon also could store sodium reversibly like lithium.
- However, the sodium doesn't have quasi-metallic property in hard carbon.(?)



- Low true density
- Safety concern
- Low initial coulombic efficiency (~80%)
- High cost

New anode (Low cost & high capacity)

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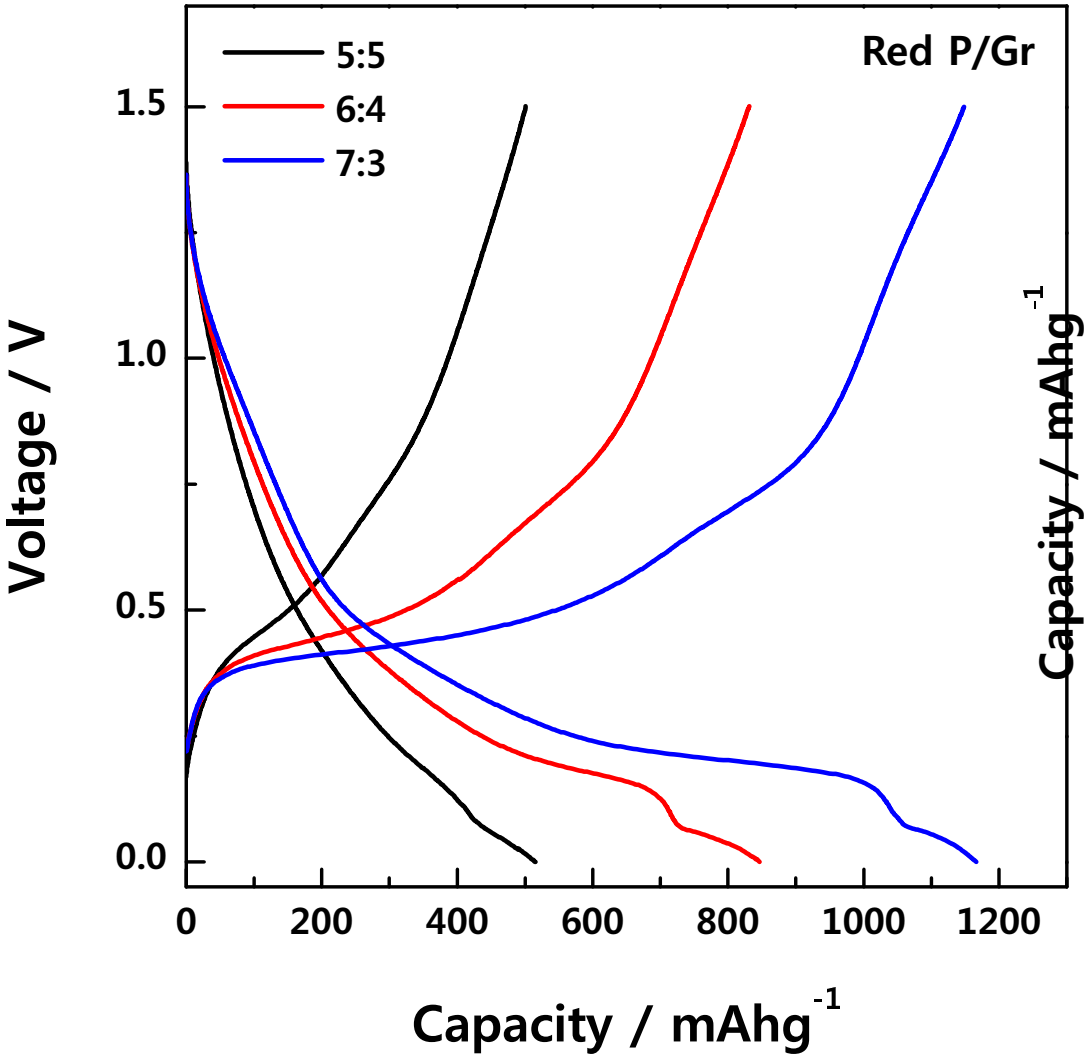
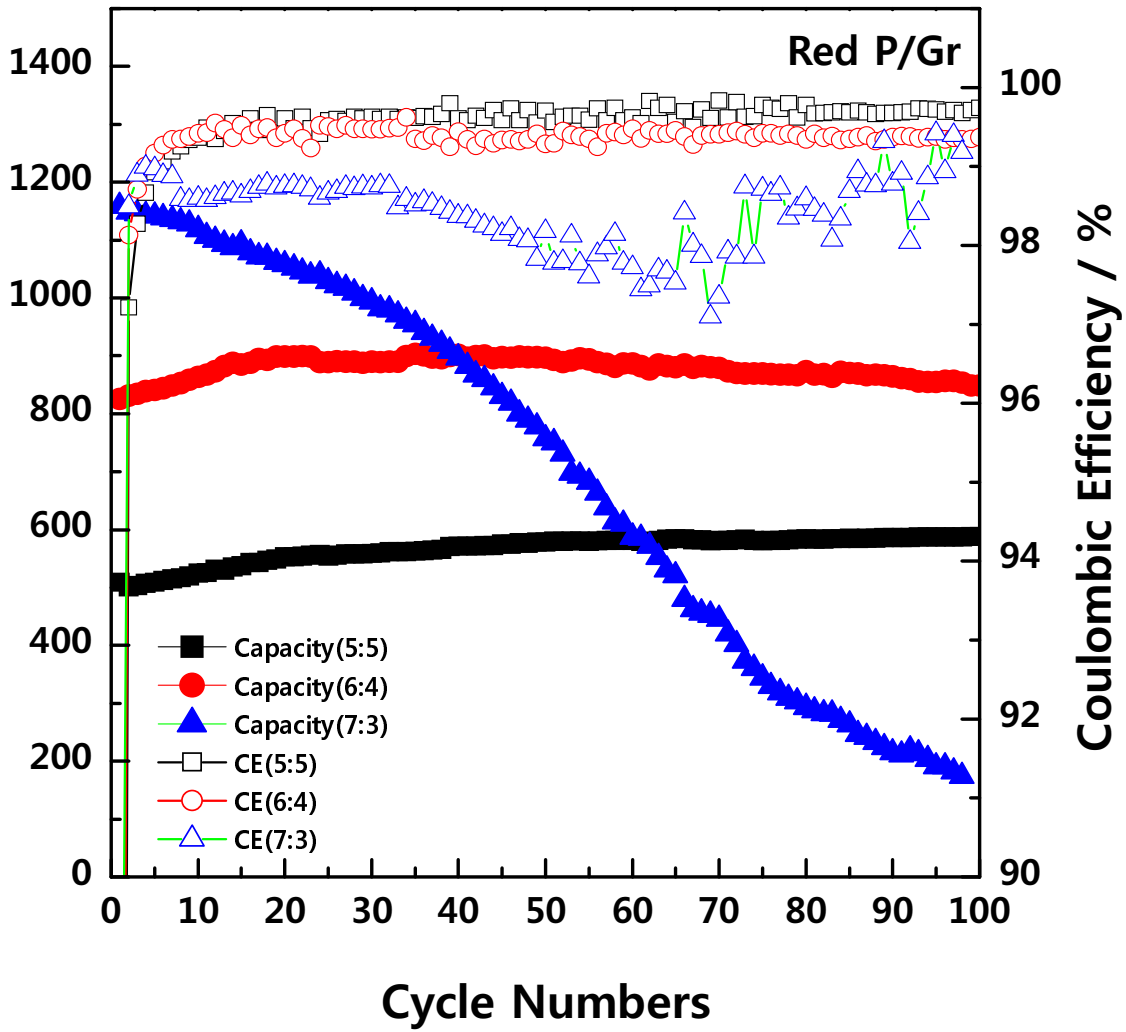
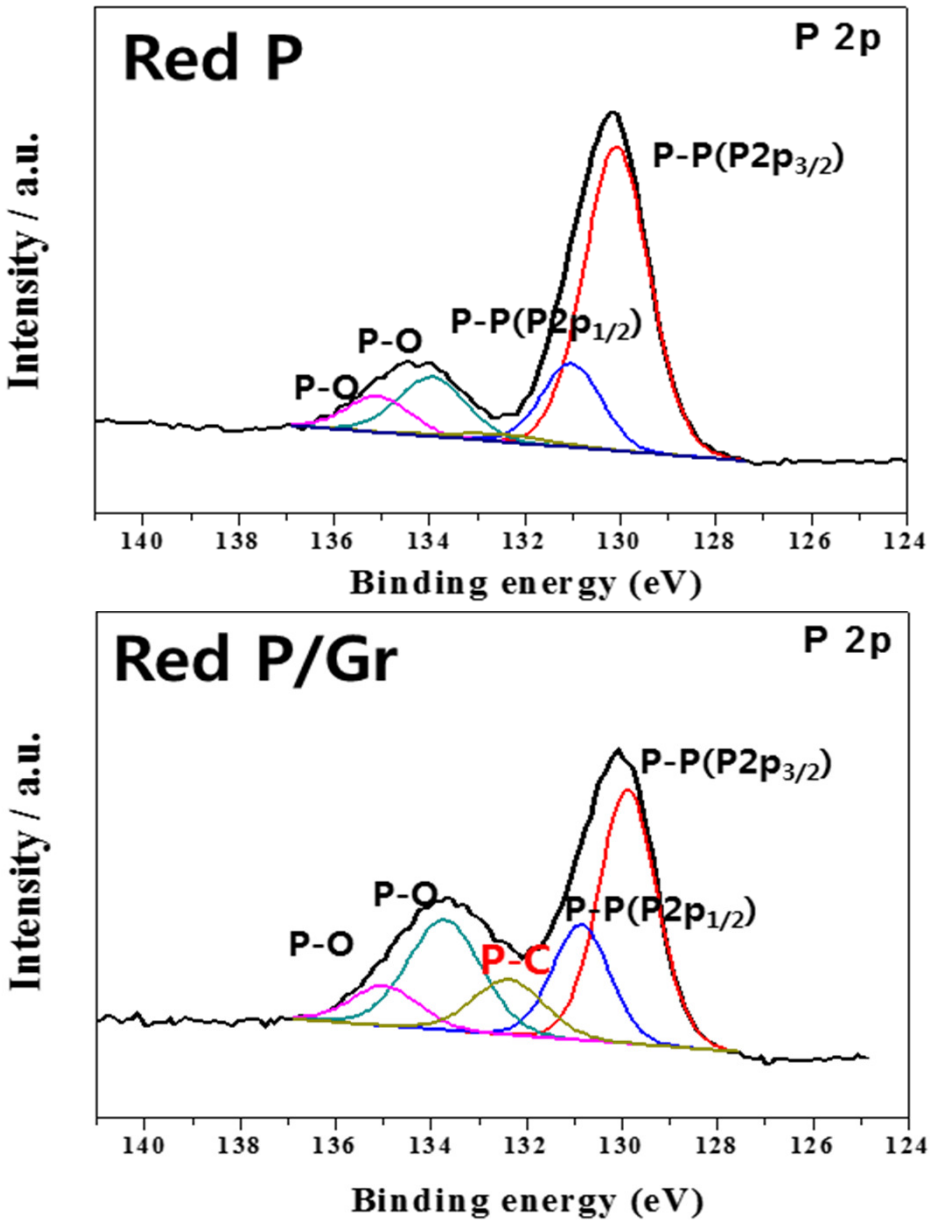
Synthesis of red P/Gr anode with higher reversible capacity

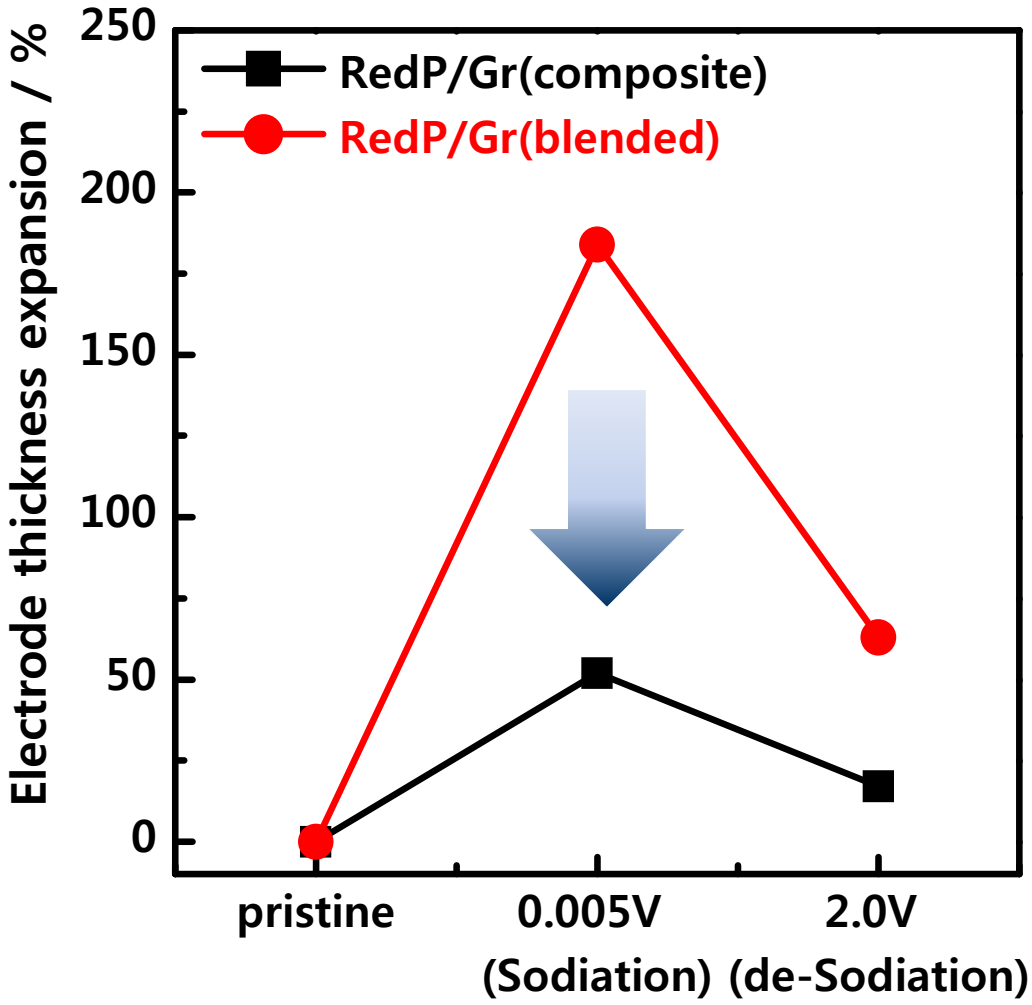




New anode (Low cost & high capacity)

Structural stabilization by P-C bonding





Energy density

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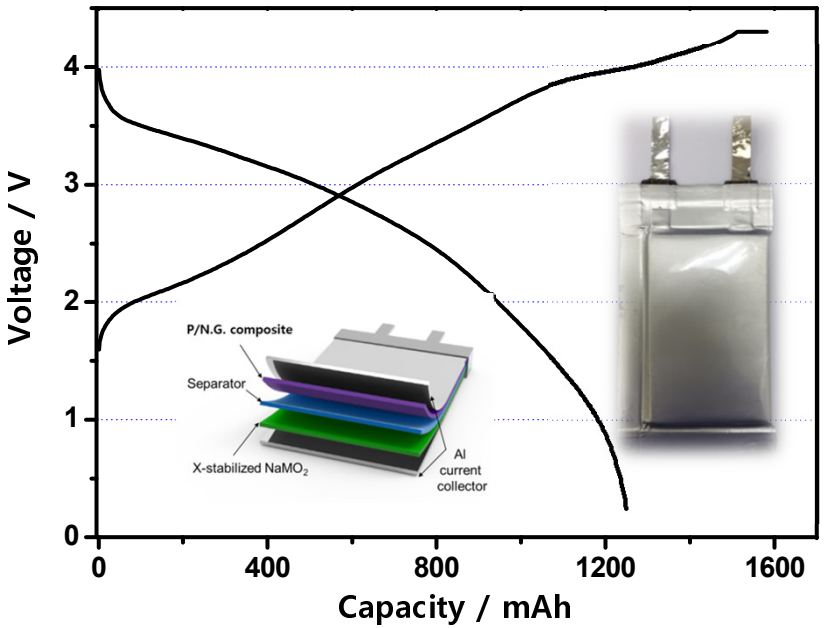
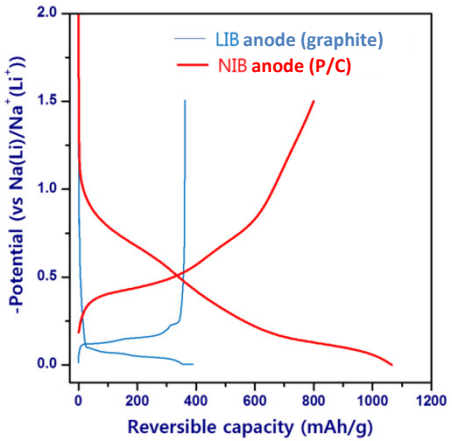
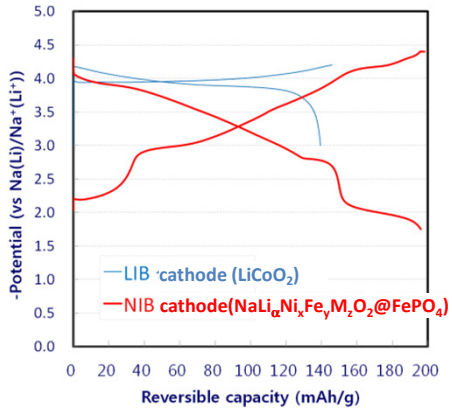
Prototype Na-Ion battery (Gen.1)



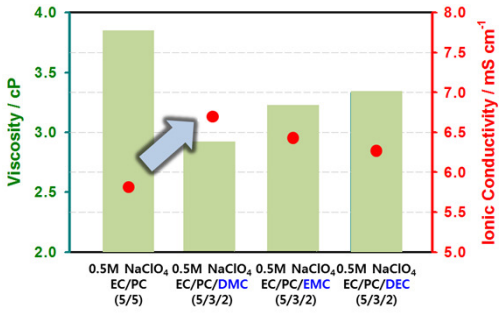
- Battery energy : 3.36 Wh
- Battery weight : 27.8g
- Battery energy density : 121 Wh/Kg
- Operating voltage range : 0.25V~4.3V



- Low cost (N.G.)/Red P



- Low cost Co-free cathode



- Low cost F-free electrolyte
- PVDF-coated PE membrane

Cyclic durability

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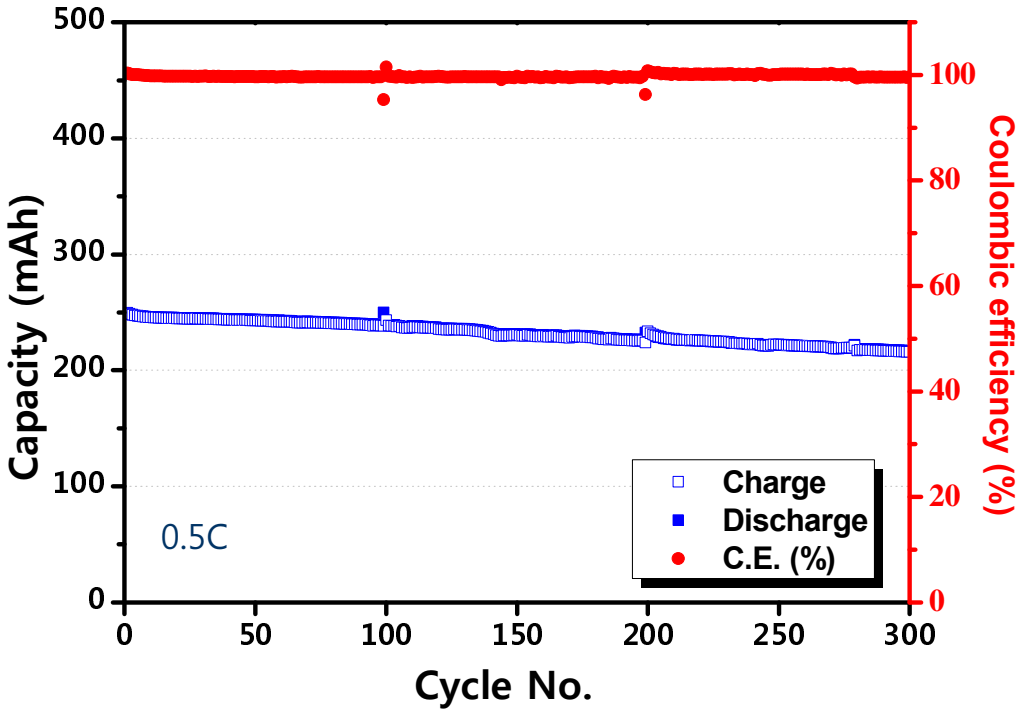
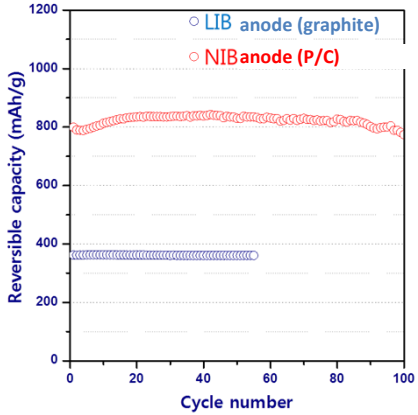
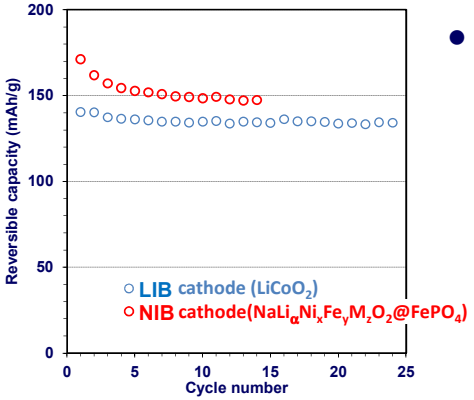
Prototype Na-Ion battery (Gen.1)

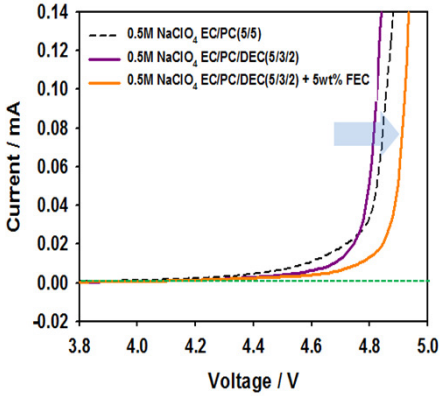




- Robust C-P bonding
- Robust binder design



- Li-stabilized structure



- High voltage stability

Low-temp. dischargeability

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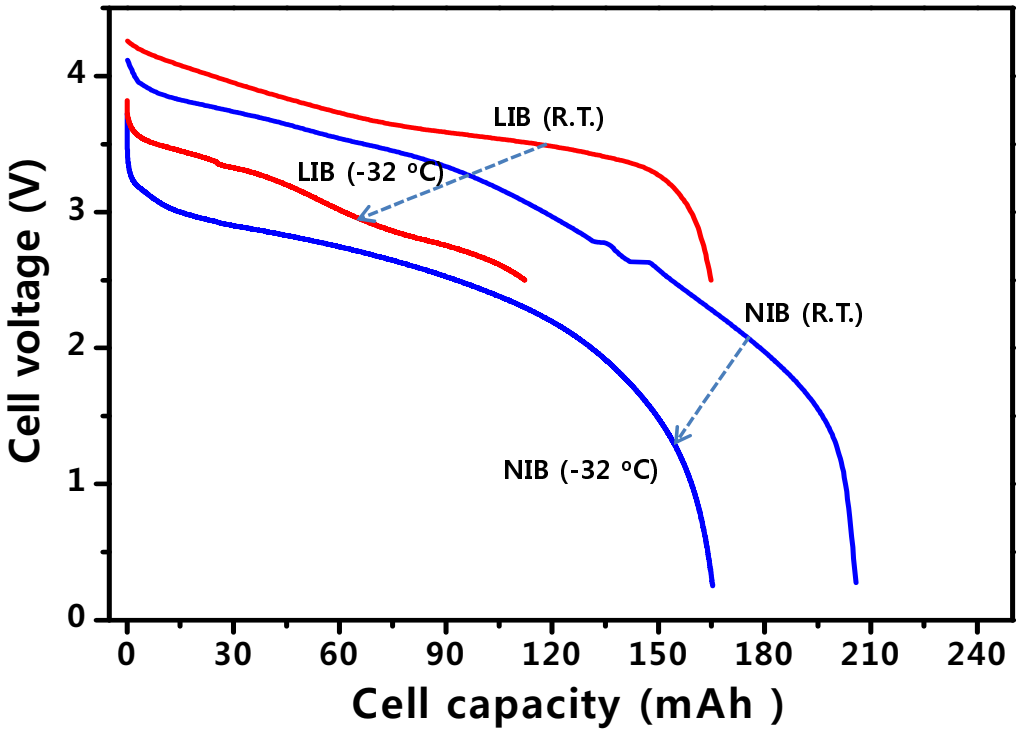
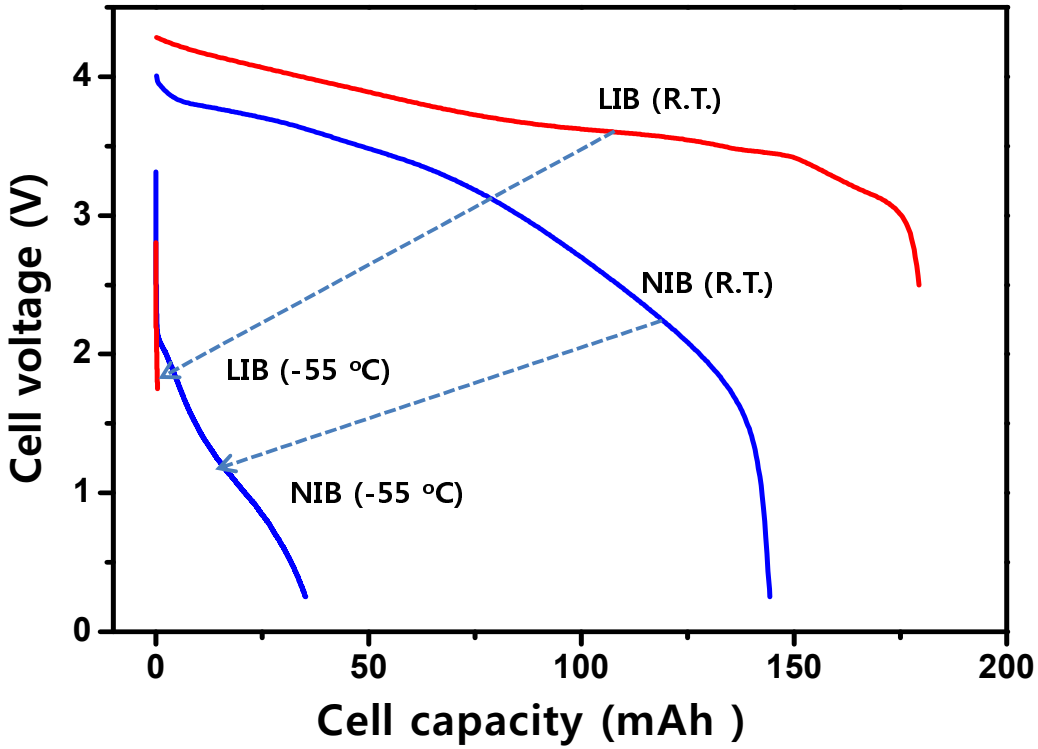
-32°C



-55°C



LIB ($C_{-32°C}/C_{R.T.}$= 68%, 12.3mΩ)
NIB ($C_{-32°C}/C_{R.T.}$= 80%, 9.6mΩ)

LIB ($C_{-55°C}/C_{R.T.}$=0%, 41mΩ)
NIB ($C_{-55°C}/C_{R.T.}$=24%, 23mΩ)

Cost

Prototype Na-Ion battery (Gen.3)

Cathode : Assuming metal precursor to be 80%

$Li_2CO_3 \rightarrow Na_2CO_3$ ($165/$4262)

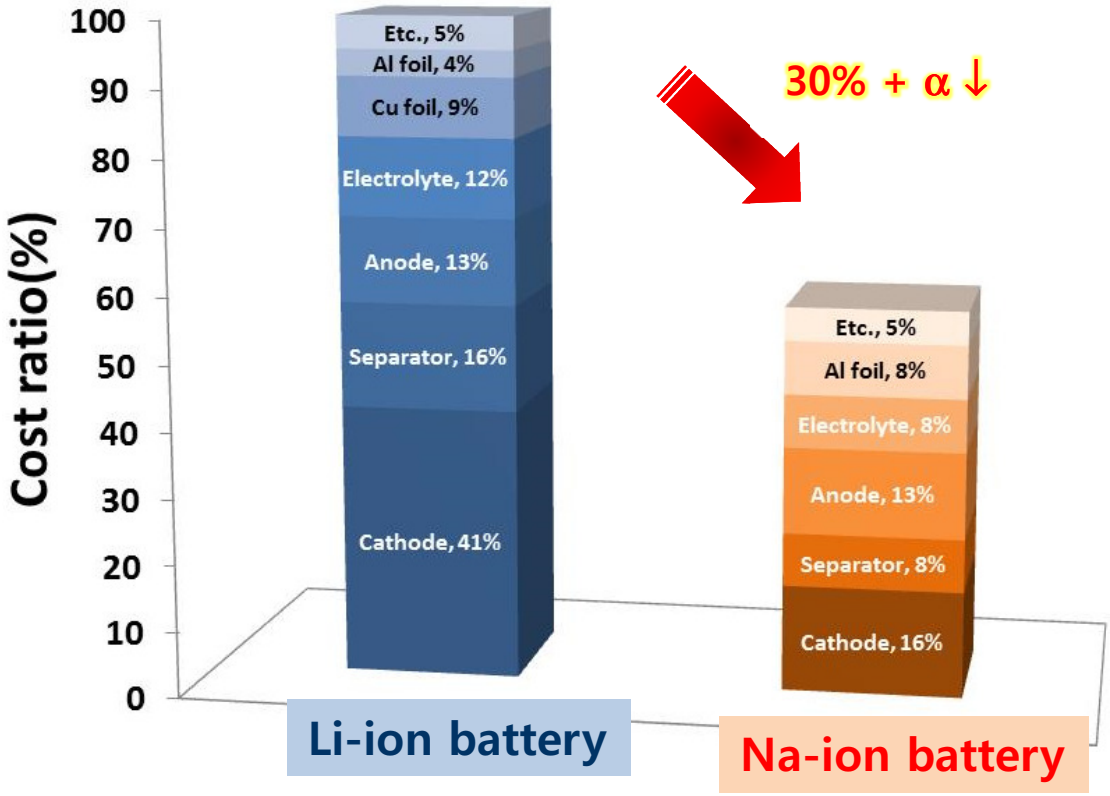
$LiCoO_2 \rightarrow NaLi_\alpha Ni_x Fe_y Mn_z O_2$ **(43% ↓)** ($20/$35)

Separator : N.A.

Electrolyte : Assuming salt cost to be 45%

$LiPF_6 \rightarrow NaClO_4$ **(74% ↓)** ($141/$543)

Parts : Anode Cu foil → Al foil **(50% ↓)**



Performance chart (SIB vs LIB)

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Performance chart

Items	SIB(KERI)	LIB (commercialized**)	Remarks
Anode material	**Expanded graphite/P**	Graphite	Lower cost
Cathode material	**$NaLi_{0.05}Ni_xFe_yMn_zO_2$ @$FePO_4$**	$LiNi_xCo_yMn_zO_2$	Lower cost
Electrolyte	**PC/X+$NaClO_4$ +FEC**	EC/DEC/L.C.+$LiPF_6$	Lower cost
Cost reduction (% ↓ $NIB/$LIB)	**~30**	-	Lower cost
Energy density (Wh/Kg)	**121**	~150**	Inferior
Cycle life (% @ 300th cy)	**87.5**	>90%	Comparable
Low temp. discharge-ability (% @ $C_{<-32°C}/C_{25°C}$)	**80%**	N.A.	Superior

**Designed for ESS

Acknowledgement

Acknowledgement

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- **KRICT : Dr. Y.G.Kang, Dr. J.D.Seok**
- **UNIST : Prof. N.S.Choi**
- **SNU : Prof. K.T.Lee**

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Thank you for attention !